Simulation of the sulfur retention in an oxy-fuel 20 MW CFB combustor.

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Abstract

Oxy-fuel combustion is a CO_2 capture technology which consists of burning the fuel with a mix of pure oxygen and recycled flue gas, mainly composed of H_2O(v) and CO_2. Therefore, after steam condensation, the CO_2 concentration in the flue gas may be enriched up to 95% (dry basis). Many of current researches are related to oxy-fuel pulverized coal combustion. However, circulating fluidized bed combustors can be a promising technology because in addition to other advantages, they have the possibility of carrying out the in situ desulfurization process via Ca-based sorbent added into the combustor which is highly dependent on the temperature and concentration of CO_2. Because under oxy-fuel combustion the sorbent can be surrounded by CO_2 concentrations ranging from 60 to 90%, the sulfation of the Ca-based sorbent can be performed at calcining (CaO solid reactant) or non-calcining conditions ($CaCO_3$ solid reactant).

A particle sulfation model has been developed to describe the limestone sulfation reaction which is carried out in two steps. The simplicity of the kinetic model permitted it to be incorporated easily in a 1.5D computational simulation model of an oxy-fuel CFB to predict the sulfur retention reached inside the boiler. The model is capable of giving important information about the oxy-coal combustion process such as longitudinal profiles of the gases (O_2, CO_2, H_2O, SO_2, etc.), char concentration distribution, combustion efficiency and sulfur retention at different operating conditions. A simulation considering the main operating variables such as temperature, sorbent reactivity, O_2 concentration fed, type of coal and the use of a desulfurization unit in the recycled flue gas was carried out to determine the most influential ones. The model is considered a useful tool to optimize the oxy-fuel combustion process in circulating fluidized bed combustors.

Keywords: Modeling, Oxy-fuel, Sulfur retention, Circulating Fluidized Bed

1. Introduction

Nowadays, there is a great public awareness about the emissions of pollutant gases into the atmosphere from large power plants. The release of CO_2 and SO_2 gases from coal combustion to generate electric power causes serious environmental problems. The former contributes to the build-up of greenhouse gases and the latter to acid rain formation. According to the IPCC 2005 [1], CO_2 capture and storage technologies could be promising to mitigate CO_2 emissions from large power plants into the atmosphere. The development of CO_2 capture technologies to obtain an outlet gas stream in energy generation processes with high CO_2 concentration seems to be one of the most reliable solutions to slow down the increase of CO_2 in the future.

Oxy-fuel combustion is a Carbon Capture technological option which consists of burning the fuel with a mix of pure oxygen and recycled flue gas which is mainly composed of CO_2. Therefore, the CO_2 concentration in the flue gas may be enriched up to 95% (dry basis) in order to be subsequently transported and stored. Nowadays, oxy-fuel combustion is still under

development and it has been not yet used commercially for CO_2 capture. Nevertheless, several large-scale demonstration boilers are planned for the future: White Rose, FuturGen, Datang Daqing and Shanxi International Energy Group CCUS projects [2]. All of them refer to pulverized coal (PC) boilers. However, circulating fluidized bed combustors (CFBCs) can be promising candidates for new coal fired power plants [3-5] because the circulation of solids can provide an effective control of the temperature in the boiler and the in situ desulfurization process can be carried out by supplying Ca-based sorbents into the combustor. The OXYCFB 300 Compostilla project was expected to start in 2018 but, nowadays, this project is considered cancelled due to lack of funding [2].

Depending on the operating conditions existing in fluidized bed (FB) combustors, the sorbent can present different behavior. Figure 1 shows the thermodynamic equilibrium curve of $CaCO_3$ calcination. As can be seen, at typical air combustion in FB (≈15% CO_2 and 850 ºC), the sorbent always calcines (R1) and thus the sulfation of the CaO, so-called indirect sulfation, takes place (R2). However, under oxy-fuel combustion, the sorbent can be surrounded by CO_2 concentrations ranging from 60 to 90 % in the FB reactor and thus the sulfur retention can be produced under indirect (R2) or direct sulfation (R3).

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad \text{(R1)}$$

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons CaSO_4 \quad \text{(R2)}$$

$$CaCO_3 + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons CaSO_4 + CO_2 \quad \text{(R3)}$$

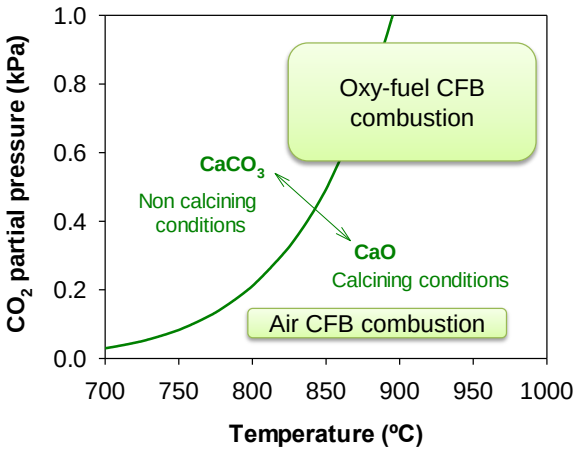

Figure. 1. Thermodynamic equilibrium curve of $CaCO_3$ calcination.

In previous studies performed in a TGA and in a batch FB to analyze the reactivity of different Ca-based sorbents, it was observed that that the highest sulfation conversions were reached at calcining conditions and the sulfation reaction was carried out in two steps, the former being faster than the latter. Therefore, a sulfation kinetic model operating under calcining conditions was developed taking into account both steps. It was assumed that the first step was controlled by the gas diffusion through the porous system of the particle and the second step by the gas diffusion through the product layer according to shrinking core model [6].

In this work, an air CFBC model (1.5D) previously developed and validated by the research group [7-9] has been adapted to oxy-fuel combustion conditions. This oxy-fuel CFBC model (1.5D) considers the recycled flue gas and the sulfation kinetic model previously developed. The simulation of this CFBC model has been capable of predicting the longitudinal profiles of the different gaseous products (O_2, CO, CO_2, H_2O and SO_2) along the boiler, the combustion efficiency and the sulfur retention reached at different operating conditions. In summary, the

simulation of the model has been very useful to know the effect of the main operating variables on sulfur retention in this type of boilers.

2. Sulfation reaction model.

The sulfation reaction model has been subject of many experimental and theoretical investigations. However, most of them are complex and their integration in a model of boiler is difficult when combustion and sulfation processes are carried out simultaneously.

In this work, a model based on the shrinking core model was proposed to predict the behavior of limestones during the sulfation reaction in oxy-fuel firing mode under calcining conditions at typical time scales and particle sizes of CFBCs. This model was chosen due to its simplicity in order to be easily incorporated into global CFBC models.

To develop this sulfation model, the techniques used for the sorbent characterization were a TGA and a batch FB. The TGA permitted the study of gas-solid reactions for long time test in differential operating conditions and the batch FB allowed the sorbent characterization in similar conditions to those existing in fluidized bed combustors, such as simultaneous calcination and sulfation, attrition, thermal shock and crackle.

It was observed that the model predicted properly the evolution of the sorbent sulfation conversion assuming that the first step of the sulfation reaction was controlled by the gas diffusion through the porous system of the particle up to the blockage of its outer pores by $CaSO_4$ formation, and the second step by the gas diffusion through the $CaSO_4$ product layer. The main equations that define the process were the following [6]:

First step: Controlled by the gas diffusion through porous system of the particle

$$t_{diff1} = \frac{\rho_{CaO}\left(R_0^3 - r_c^3\right)\left(R_0 - r_c\right)}{3D_0 C_{SO2} R_0 r_c \left(Z-1\right)}\left(\frac{1}{\varepsilon_0 - x_l\left(1-\varepsilon_0\right)\left(Z-1\right)} - \frac{1}{\varepsilon_0}\right) \qquad t_{diff1} < t_1 \qquad (1)$$

$$X_{s,\max} = \frac{\varepsilon_0}{\left(1-\varepsilon_0\right)\left(Z-1\right)} \qquad X_s = x_l \frac{\left(R_0^3 - r_c^3\right)}{R_0^3} \qquad (2)$$

$$D_e = D_0\, \varepsilon^2 \qquad (3)$$

Second step: Controlled by the gas diffusion through product layer.

$$\frac{t_{diff2} - t_1}{\tau_{diff2}} = 3\left[\left(1 - \frac{X_1}{X_{s,\max}}\right)^{2/3} - \left(1 - \frac{X_s}{X_{s,\max}}\right)^{2/3}\right] - 2\left(\frac{X_s - X_1}{X_{s,\max}}\right) \qquad t_{diff2} > t_1 \qquad (4)$$

$$\tau_{diff2} = \frac{\rho_{CaO} X_{\lim} d_p^2}{24 D_s C_{SO2}} \qquad (5)$$

The transition from the first to the second step is produced when $D_e(\varepsilon)=D_s$ which corresponds to a time, t_1 , and a sulfation conversion, X_1. Figure 2 shows the predictions of model at different operating conditions using the kinetic parameters obtained for Granicarb limestone.

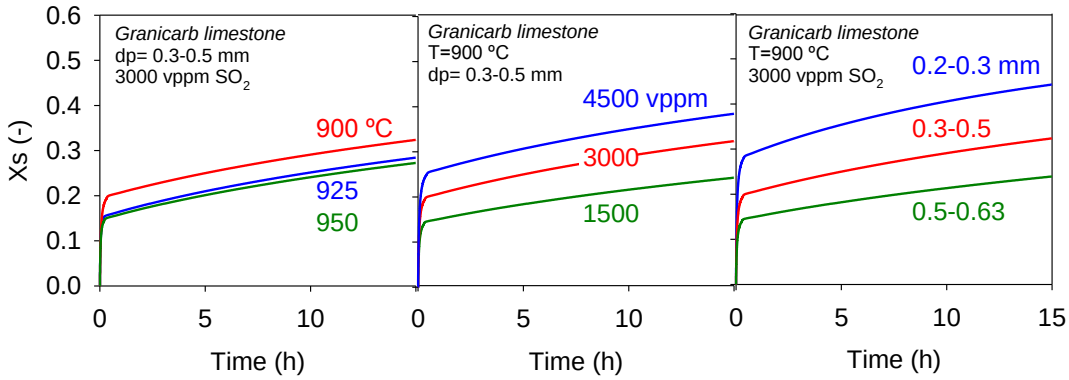

Figure 2. Sulfation conversion curves predicted by the sulfation reaction model.

3. Mathematical model of oxy-fuel CFBC (1.5D)

The mathematical model describes the behavior of a CFBC referred to coal combustion and sulfur retention processes in oxy-fuel mode. The 1.5D model considers both radial and longitudinal concentration profiles and assumes steady-state and isothermal operation at macroscopic level. The model integrates different sub-models to describe the main processes occurring inside the boiler as hydrodynamic, carbon combustion and sulfur retention. Figure 3 shows the scheme of the CFBC considered.

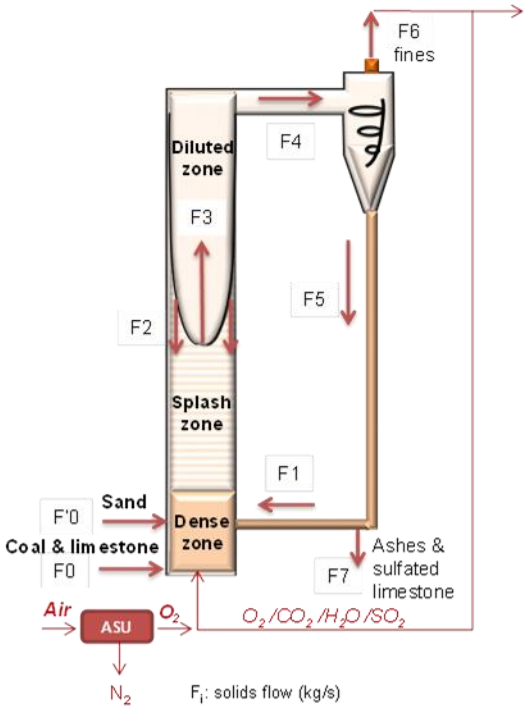

Figure 3. Scheme of the CFB boiler.

3.1. Hydrodynamic sub-model

The hydrodynamic characteristics of the CFBC are based on the works of Johnson et al. [10], Johnson and Leckner [11] and Pallares et al. [12]. The riser is divided into three different zones: bottom, similar to a bubbling bed; splash, with a predominant homogeneous particle clustering flow; and transport zone, with a core-annulus structure.

The bottom zone consists of a bubble and emulsion phase where the total flow is assumed to be the sum of three flows: the flow in the particulate phase, the visible bubble flow, and the throughflow, that is, a flow through and between the bubbles. Likewise it was supposed that the average voidage is constant in the entire zone and the emulsion phase remains under minimum fluidization conditions.

In the splash and transport zones, the vertical distribution of solids was determined by means of an exponential decay model. The solid concentration was assumed to be the sum of the contribution from a cluster phase and a dispersed phase:

$$\rho = (\rho_b - \rho_{d,b})\exp\left[-a(h - H_b)\right] + \rho_{exit}\exp\left[K(H_0 - h)\right] \quad (6)$$

$$\rho_{d,b} = \rho_{exit}\exp\left[K(H_0 - H_b)\right] \quad (7)$$

The upper level of the splash zone is defined as the height where the two terms (contributions of cluster and dispersed phases) of equation (1) are equal. The decay constants in the splash, a, and transport, K, zones as a function of the operating conditions, and are calculated with the equations:

$$a = 4u_t / u \quad (8)$$

$$K = 0.23/(u - u_t) \quad (9)$$

The solution of the hydrodynamic model gives at each height of the riser the mean voidage, annulus and core voidages, core radius, upward solids flow in the core, downward solids flow in the annulus and external circulation of solids flux.

3.2. Coal combustion sub-model

The carbon combustion model takes into consideration all the processes that coal particles undergo when they are fed into the combustor such as drying, devolatilization and volatiles combustion, and char combustion. The model developed by de Diego et al. [13] is used to calculate the volatile generation rate of the coal. In this model the drying and pyrolysis of coal particles are assumed to be a coupled process controlled by the kinetics of devolatilization and the heat transferred to and through the particles. The volatiles generated during devolatilization are considered as a mixture of H_2O, CO, CO_2, H_2, CH_4, C_2H_4 and C_3H_8. The excess of C is considered as elementary C, which is instantaneously oxidized to CO. The volatile combustion process is modelled considering different chemical reactions with their corresponding reaction rates [14].

*Char combustion***.** To fulfill mass balances and determine carbon combustion efficiencies in a CFB with shrinking particles, it is necessary to develop population balances of char particles in the different zones of the CFBC (bottom, splash, and transport zones).

For discrete particle size distributions, the population balances of char particles in the bottom and splash zones, involve the following system of equations [15]:

$$P_3(r_i)\Delta r_i = \frac{W_{cl,i}}{W_{cl}} == \frac{F_i^*\Delta r_i + W_{cl,i+1}\mathrm{r}_{\mathrm{shrink}}(r_{i+1})\dfrac{\Delta r_i}{\Delta r_{i+1}} + \sum P_f(r_i)W_{cl,i}k_f r_i}{F_3\Delta r_i + W_{cl}\mathrm{r}_{\mathrm{shrink}}(r_i) + 3W_{cl}\mathrm{r}_{\mathrm{shrink}}(r_i)\Delta r_i / r_i + W_{cl}k_f r_i} \quad (10)$$

where $F^*_i = F_{0,i} + F_{1,i} + F_{2,i}$

The population balances of char particles burning in each compartment j of the transport region involve the following expression for the core region:

$$P_{3,j}(r_i)\Delta r_i = \frac{F_{3i,j}}{F_3} = \frac{F_{3i,j-1}\Delta r_i + W_{cc,i+1,j}\mathrm{r}_{\mathrm{shrink}}(r_{i+1})\dfrac{\Delta r_i}{\Delta r_{i+1}} + \sum P_f(r_i)W_{cc,i,j}k_f r_i}{F_{3,j}\Delta r_i + W_{cc,j}\mathrm{r}_{\mathrm{shrink}}(r_i) + T_{3,j}\Delta r_i + 3W_{cc,j}\mathrm{r}_{\mathrm{shrink}}(r_i)\Delta r_i / r_i + W_{cc,j}k_f r_i} \quad (11)$$

The solution of the population balances in the bottom+splash and transport regions allows us to determine the carbon flow rates in all streams of the process.

For the solution of char population balances, it is necessary to know the individual shrinking rates (r_i) of the char particles. Assuming the shrinking unreacted particle model, with mixed control by chemical reaction and mass transfer in the gas film and with a first order of reaction, the shrinking rates of char particles are given by the expression:

$$\mathrm{r}_{\mathrm{shrink}}(r_i) = \left(-\frac{\mathrm{dr}}{\mathrm{dt}}\right) = \frac{12\mathrm{C}_{\mathrm{O_2}}}{\mathrm{j_c}\rho_c(1/\mathrm{k_c} + \mathrm{d_p}/\mathrm{ShD_g})} \quad (12)$$

The term C_{O2} indicates the effective oxygen concentration around the char particles burning at any point of the boiler. Therefore, the population balances must be solved at the same time as the oxygen profiles in the boiler. In addition, the following equation is used for the combustion process according to the kinetic constants determined for the coal used in this work:

$$k_c = T_s \exp(-75.4 / RT_s) \quad (13)$$

The solution of the mathematical model implies the simultaneous convergence of the char particle population balances and the oxygen profile in the riser. Since the oxygen concentration at each height depends on the char and volatile combustion, mass balances for the char, oxygen and volatiles is simultaneously solved.

3.3. Sulfur retention sub-model

Sulfur retention (SR) rate inside the CFB boiler depends on both the SO_2 generation rate and sorbent sulfation rate (which depends on the sorbent characteristics). Both processes can be produced in the different zones of the boiler (bottom, splash and diluted zone).

SO_2 generation rate is a function of the coal combustion rate which includes the sulfur coming from both volatiles and char. Therefore, the longitudinal profile of SO_2 release along the riser is a direct consequence of the coal combustion process and is determined by the previous combustion model.

The SO_2 retention rate strongly depends on the SO_2 concentration existing at the different zones of the boiler. This concentration is conditioned by the SO_2 generation process and by the sulfation capability of the sorbent.

In each location of the boiler with a given SO_2 concentration, the mean reactivity is defined as a function of the mean solids residence time (τ), assuming perfect mixing of the solids in the whole bed.

$$\overline{\left(\frac{dX_s}{dt}\right)} = \int_0^\infty \left(\frac{dX_S}{dt}\right) E(t)dt \qquad E(t) = \frac{e^{-t/\tau(r_i)}}{\tau(r_i)} \quad (14)$$

The mean residence time of the sorbent is defined by solving the hydrodynamic model previously developed. The sorbent reactivity was calculated using the sulfation model of two step above-mentioned and defined by the equations (1) (2) (3) (4) and (5) where the first step was controlled by the gas diffusion through porous system of the particle and the second step by the gas diffusion through product layer.

The calculation of sulfur balance is solved at the different compartments from the bottom to the top of the riser. Therefore, the SO_2 concentration at the outlet gas stream is known. Finally, the sulfur retention in the boiler is given by the following equation considering the sulfur fed from the coal and the SO_2 obtained at the outlet gas stream.

$$R_S = \frac{\left(F_{0,coal} x_{S,coal} / M_S\right) - QC_S}{F_{0,coal} x_{S,coal} / M_S}.100 \quad (15)$$

Once the sulfur retention is calculated, the mean sulfation conversion the sorbent can be determined by means of the following expression,

$$\overline{X}_s = \frac{R_s}{Ca / S} \quad (16)$$

After solving both the carbon combustion and the sulfur retention processes, the model is able to predict the longitudinal profiles of the different gaseous products (O_2, CH_4, C_2H_4, C_3H_8, H_2, CO, CO_2, H_2O and SO_2) along the boiler. In addition, the model predict the concentration and particle size distribution of the char particles in the different locations of the boiler as well as the combustion efficiency and sulfur retention obtained at the different operating conditions.

4. Simulation

Once the mathematical model 1.5D was developed, the simulation of the oxy-CFB combustor model focused on the sulfur retention process at different operating conditions was carried out. Table 1 shows the main input data used as reference case in the model simulation.

Table 1. Simulation conditions used in the reference case.

	Units			Units	
Power	[MW_t]	20	**Coal composition**		**Anthracite**
			Moisture	wt.-%	2.3
Furnace dimensions			Ashes	wt.-%	31.8
Diameter	[m]	2.5	C	wt.-%	52.6
Height	[m]	20	H	wt.-%	1.7
			N	wt.-%	0.93
Cyclone dimensions			S	wt.-%	1.52
diameter	[mm]	875	LHV	[MJ/kg]	20
			Particle size		
Operating parameters					n=2
			Coal distribution		(Rosin - Rammler)
Temperature	[ºC]	900	Sorbent	[mm]	0.2
Linear velocity	[m/s]	5.0			
Pressure drop	[Pa]	25000	**Granicarb kinetic parameters**		
Inlet O_2	[vol.%]	25	D_0	[m^2/s]	$1.35\ 10^{-5}$
O_2 excess	[vol.%]	5	e	(μm)	29
Ca/S	[mol/mol]	2	D_s	[m^2/s]	$1.5\ 10^{-8}$
Total solids flow in	[kg/h]	1200			

Hydrodinamic sub-model defines the solids distribution inside the reactor taking into account the operating conditions used (temperature, gas velocity, pressure drop, etc.) and the different height of zones (bottom, splash and diluted). Figure 4 shows the profiles of solids

concentration (ρ) in the combustor for the reference case. Likewise, hydrodynamic also determines the coal and char distribution along the combustor and thus the distribution of the different gases. Figure 5 shows the profiles of gases concentration in the combustor for the reference case. As can be seen, an increase in CO_2 concentration together with a decrease in O_2 concentration is produced in the splash zone because the majority of the combustion process takes place in that zone, which combines high solids and oxygen concentrations. Regarding SO_2 gas, a decrease of SO_2 concentration along the diluted zone is observed as a consequence of the sulfur retention process which prevails over SO_2 generation in that zone.

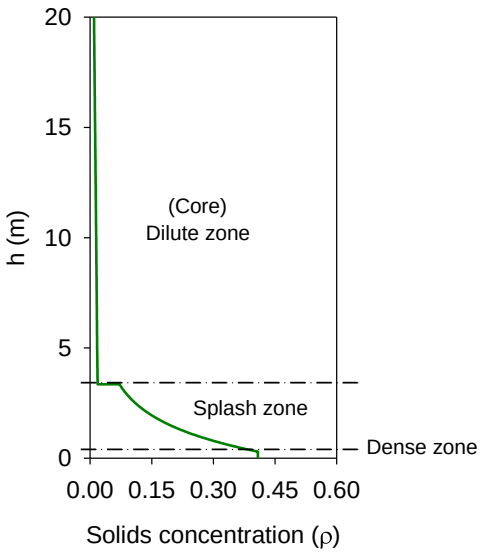

Figure 4. Solids concentration profiles.

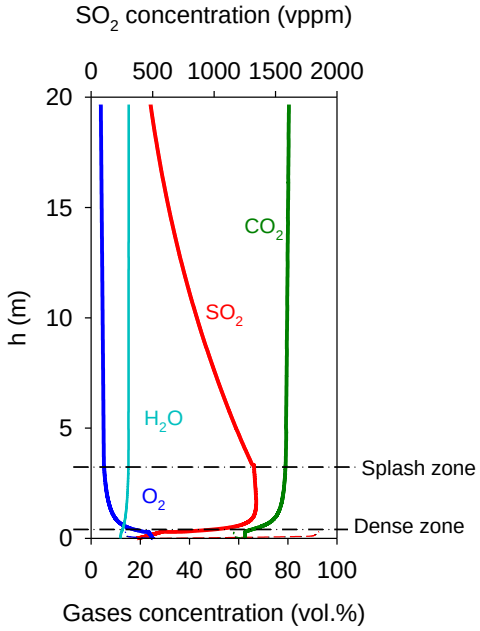

Figure 5. Gases concentration profiles.

4.1. Effect of the temperature

As stated above, the conditions exiting in the boiler can lead to a different behavior of the sorbent. Therefore, depending on the temperature and the CO_2 concentration in the flue gas recirculation is likely to find conditions inside the boiler in which the sorbent could calcine or not.

In Figures 6a and 6b are represented the SO_2 profiles and sulfur retention values obtained in the simulation at different temperatures ranging from 850 to 950 ºC, that is, from non calcining to calcining conditions. It was observed that the highest sulfur retentions are reached operating under calcining conditions. This can be attributed to the fact that the porosity of the calcined limestone (CaO) is much higher than that of the raw limestone ($CaCO_3$) and thus, SO_2 can easily diffuse through the porous system of the particle reaching higher sulfation conversions. In addition, an optimum temperature was found to be around 900ºC. This is in agreement with the results obtained in previous works [16-18].

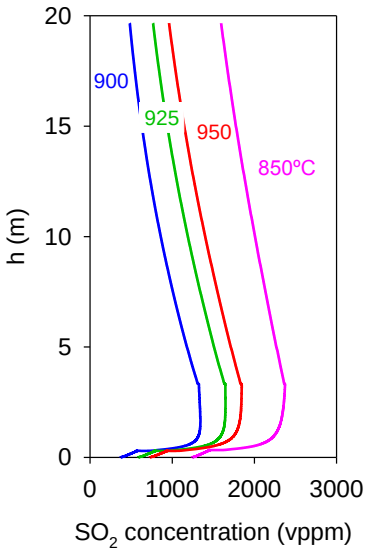

Figure 6a. SO_2 profiles at different temperatures.

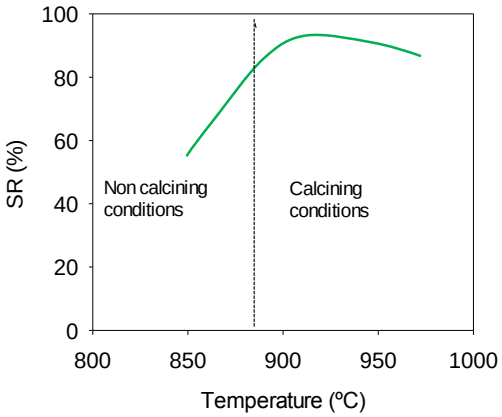

Figure 6b. Effect of temperature on sulfur retention.

4.2. Effect of the limestone reactivity

Another remarkable parameter to take into account in order to work in CFBCs is selecting an adequate Ca-based sorbent to perform the desulfurization process. In this section, the variation of the kinetic parameters determined in a previous work [6] for the first and second steps has been simulated. Figures 7a and 8a show the sulfation conversion curves of the limestone used for the first and second sulfation steps assuming that they present a maximum sulfation conversion ($X_{s,max}$) nearly 0.52. Figures 7b and 8b illustrate the results obtained in the simulation at different Ca/S molar ratio.

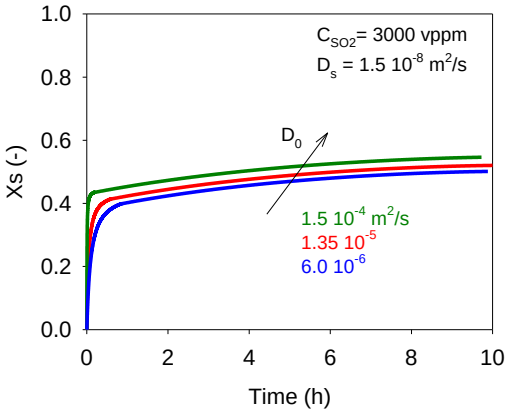

Figure 7a. Sulfation conversion curves of the limestone at different diffusional coefficients, D_0.

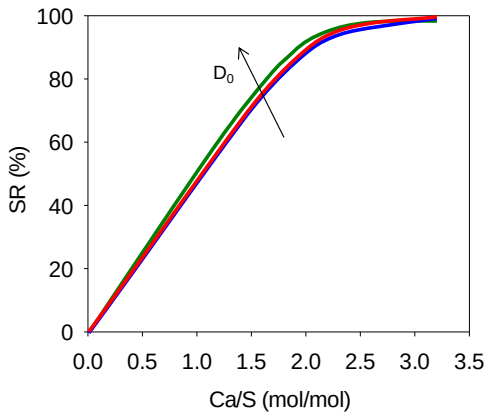

Figure 7b. Effect of D_0 on sulfur retention at different Ca/S molar ratio.

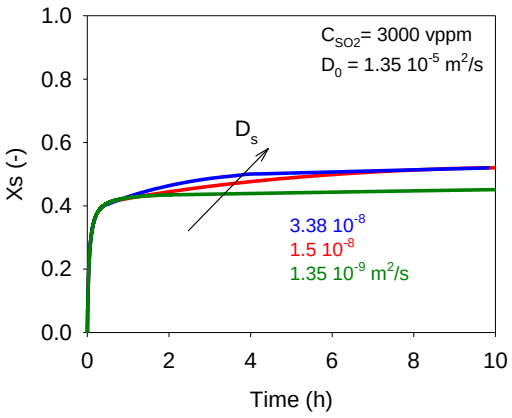

Figure 8a. Sulfation conversion curves of the limestone at different diffusional coefficients, D_s

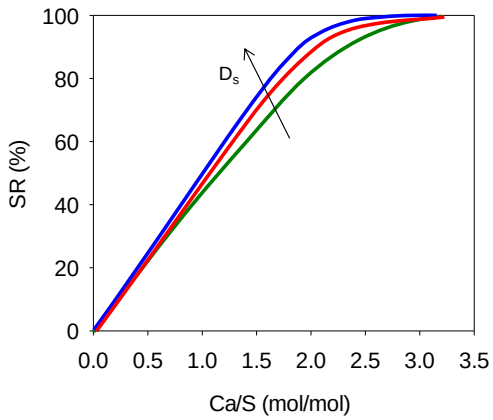

Figure 8b. Effect of D_s on sulfur retention at different Ca/S molar ratios

As it was expected, higher the Ca/S molar ratio leads to higher sulfur retention values. Moreover, the higher the diffusional coefficient, the higher the sulfur retention values since an increase in the diffusional coefficients is associated with an increase in the limestone reactivity. Likewise, it was observed that the influence of the diffusional coefficient of the second step has more relevance than those of the first step, corroborating the results reported by other authors about the importance of the residual activity of the sorbent [19].

4.3. Effect of the inlet oxygen concentration

An important feature in oxy-fuel combustion is the O_2/CO_2 ratio in the inlet gas stream. It is known that a higher inlet O_2 concentration leads to reducing the boiler size, and therefore capital expenses, and to reducing the recycled flue gas which diminishes energetic penalty [20].

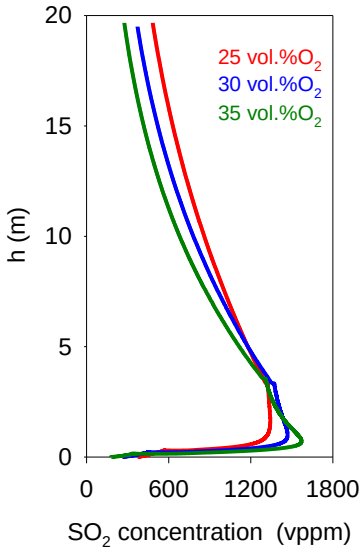

Figure 9a. SO_2 profile generated in the combustor at different inlet O_2 concentration.

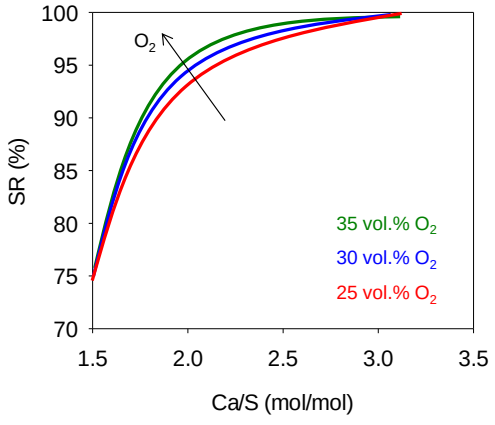

Figure 9b. Effect of inlet oxygen concentration on sulfur retention at different Ca/S molar ratios

In this section, the simulation of the effect of O_2 concentration entering the reactor on the sulfur retention is analyzed. Simulation tests with typical inlet O_2 concentrations from 25 to

35 vol.% were performed, setting an outlet O_2 concentration around 4 vol.%. As can be seen in Figures 9a and 9b, an increase in O_2 concentration causes an increase in coal feeding leading to higher SO_2 concentration inside the combustor and consequently higher sulfur retention.

4.4. Effect of the type of coal.

One of the advantages of the CFBC is the high versatility that they present to burn different types of fuel. This technology is feasible to burn both low reactivity coals, as anthracites, and high reactivity coals, as lignite. Likewise, coals with low heating value due to their high ashes content and even biomass can be also processed in CFBCs.

In this section, the simulation of three different coal ranks ranging from lignite to anthracite was carried out. Table 2 gives the proximate and ultimate analysis of the coals used.

It is worth mentioning the different sulfur content of the coal used, lignite having the highest content (5.91 %) and bituminous having the lowest content (0.8 %). The operating conditions simulated were the same as those of the reference case.

Table 2. Ultimate and proximate analysis of the coals used.

	Anthracite	Lignite	Bituminous
Proximate analysis (%wt)			
Humedad	2.3	12.6	5.2
Cenizas	31.7	25.2	12.9
Volátiles	5.6	28.7	32.7
C Fijo	60.4	33.6	49.2
Ultimate analysis (%wt, d.b.)			
C	61.02	51.95	69.2
H	1.71	2.85	4.3
N	0.95	0.74	1.6
S	1.55	5.91	0.8
LHV* (kJ/kg)	21807	16252	25398

According to Figure 10, to reach sulfur retention values close to 90-95 %, using lignite as fuel, three or six times more limestone should be fed compared to anthracite and bituminous coal which would imply an increase in the solids waste generation ($CaSO_4$).

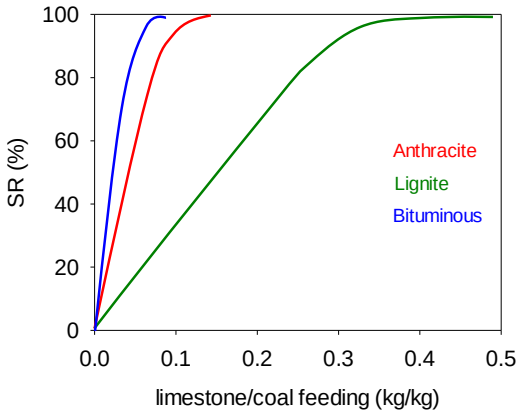

Figure 10. Dependence of sulfur retention with the limestone/coal feeding ratio for different coals.

In Figure 11 are plotted the SO_2 concentrations emitted at the exit of the combustor. It was observed that he SO_2 generated from lignite combustion was higher than that from anthracite and this latter higher than that from bituminous coal.

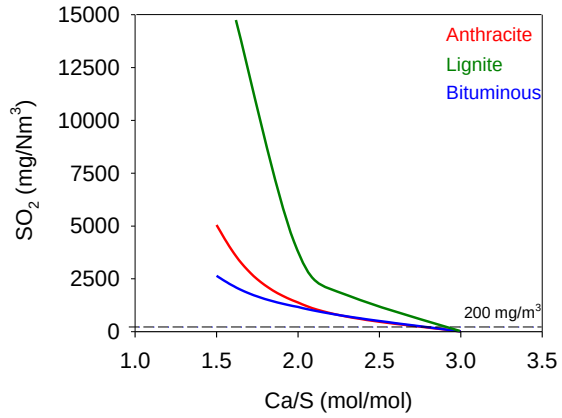

Figure 11. SO_2 concentration as a function of the Ca/S molar ratio for different coals.

According to data published by Vattenfall [21], to get a CO_2 stream with medium level of quality in order to be subsequently transported, a flue gas stream with a SO_2 concentration lower than 200 mg/Nm^3 must be needed. Last proposals made by the Dynamis study regarding the gas composition are more restricted. SO_2 concentration in the CO_2 stream must reach values below 100 vppm [22]. Therefore, from the results obtained in the CFBC simulation (see Figure 11), it can be concluded that if a Ca/S molar ratio of 2.5-3 was fed into the combustor, the use of a desulfurization unit after the oxy-fuel combustion process to fulfill with the transport requirements would not be needed.

4.5. Effect of using a desulfurization unit in the recycled flue gas.

The flue gas recirculation to control the operating temperature and inherently the inlet O_2 concentration is one of the main characteristics of the oxy fuel combustion processes. This recycled flue gas can previously be cleaned, in this case being almost free of SO_2, to avoid operationg problems related to the material corrosion.

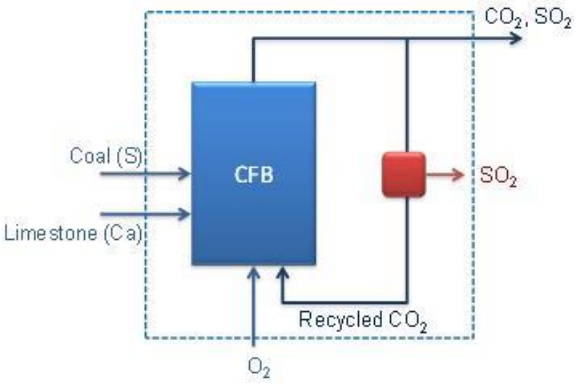

Figure 12a. Scheme of a CFB combustion system without SO_2 recirculation

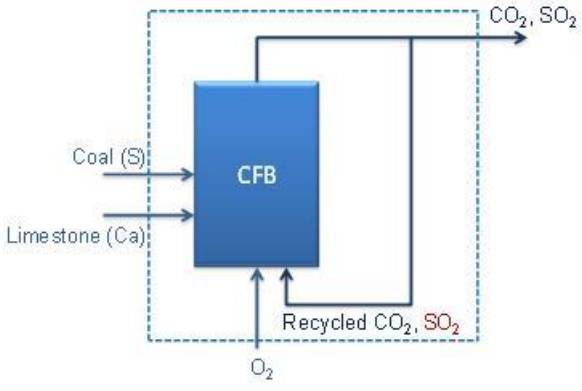

Figure 12b. Scheme of a CFB combustion system with SO_2 recirculation

Up to now, in the simulation tests performed, SO_2 and CO_2 from flue gas has been considered to be recycled together and thus an increase in SO_2 concentration inside the boiler was produced. In this section, it has been assumed that there was a cleaning step, i.e., a desulfurization unit, in the recycled flue gas to completely remove the SO_2 from the

recirculation stream (see scheme of Figure 12a). The results obtained in this simulation were compared to the reference case (see scheme of Figure 12b).

In Figure 13, the sulfur retention using or not using a desulfurization unit is shown as a function of the Ca/S molar ratio. As can be seen, the highest sulfur retention values were reached when the desulfurization unit was not used. Nevertheless, SO_2 emissions were also the highest (see Figure 14). This fact was because the SO_2 concentration inside the boiler was higher and thus the sulfation reaction rate was increased. Based on these results, to operate using anthracite as fuel and Granicarb limestone as sorbent, a molar ratio close to 2.5-3 would be needed to fulfill with the requirements of CO_2 transport commented above.

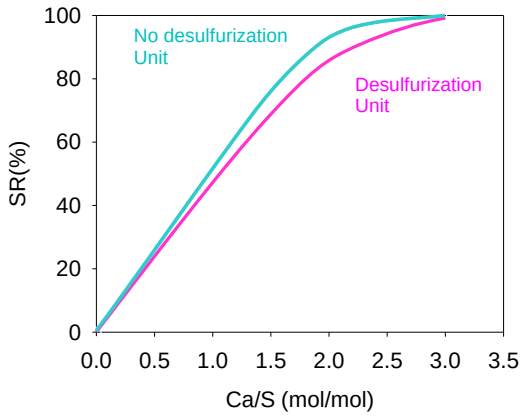

Figure 13. Sulfur retention values reached using or not using a desulfurization unit in the recycled flue gas

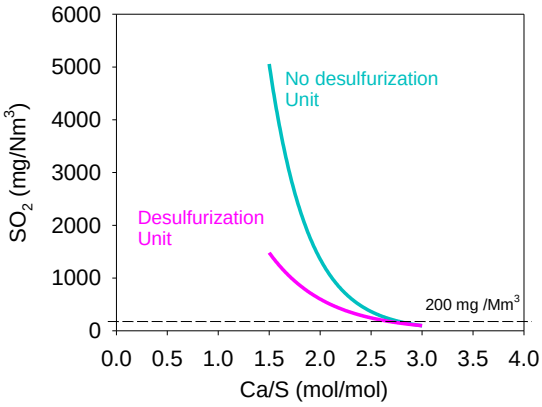

Figure 14. SO_2 concentration obtained using or not using a desulfurization unit in the recycled flue gas.

5. Conclusions

The simulation of a CFBC under oxy-fuel combustion conditions has allowed us to know the effect of the main operating variables on sulfur retention process.

On the one hand, temperature, type of coal (especially sulfur content of the coal) and sorbent reactivity has been found to be the most influential parameters affecting sulfur retention process. On the other hand, inlet O_2 concentration had a minor effect on the sulfur retention.

In order to reach high sulfur retention values and to fulfil with the requirements of CO_2 transport, it would be necessary to operate in calcining conditions, especially at 900 ºC, and with Ca/S molar ratio close to 2.5 – 3 such that a desulfurization unit would have not to be used from the viewpoint of the sulfur retention process.

Acknowlegments

This work has been supported by The Spanish Ministry of Science and Innovation (MICINN, Project: CTQ2008-05399/PPQ) and by FEDER. M. de las Obras-Loscertales thanks to MICINN for the F.P.I. fellowship.

Nomenclature

a	decay constant (m^{-1})
C	gas concentration (kmol m^{-3})
d_p	particle diameter (m)
D_g	diffusivity (m^2 s^{-1})
D_e	effective diffusivity (m^2 s^{-1})
T_s	char surface temperature (K)
T_3	flowrate of transmitted carbon from the core to annulus (kg s^{-1})
u	superficial gas velocity (m s^{-1})
u_t	single particle terminal velocity (m s^{-1})

D_0 the porous system gas diffusion coefficient ($m^2\ s^{-1}$)
D_s the product layer gas diffusion coefficient ($m^2\ s^{-1}$)
E(t) function of the mean solids residence time (s^{-1})
$F_{0\text{-}7}$ carbon flow rates (kg s^{-1})
$F_{0,coal}$ coal feeding (kg s^{-1})
h height (m)
H_b height of bottom region (m)
H_o height of riser (m)
j_c carbon fraction in the char
k_c apparent kinetic constant for surface reaction (m s^{-1})
k_f fragmentation rate constant (m s^{-1})
K transport region decay constant (m^{-1})
M_s sulfur atomic weight (g mol^{-1})
$P_{0\text{-}7}$ normalized size distribution function of the char stream (m^{-1})
P_f size distribution function on mass basis of the fragments (m^{-1})
r char particle radius(m)
r_c radius of unreacted core (m)
r_i mean radius of particles in population i (m)
$r_{shrink}(r_i)$ shrinking rate of char particles of size r_i
$(-r_i)$ combustion rate of gas I (kmol $m^{-3}\ s^{-1}$)
R gas constant (J $mol^{-1}\ K^{-1}$)
R_0 initial particle radius of the limestone (m)
SR sulfur retention (%)
Sh Sherwood number
t time(s)
t_1 the transition time between the first and the second step in the limestone sulfation reaction (s)
W mass (kg)
x_l sulfur conversion of the product layer
$x_{s,coal}$ sulfur mass fraction of coal
X_1 the sorbent sulfation at t1
X_s sulfation conversion
$X_{s,max}$ maximum sulfation conversion
Z the molar volume ratio of $CaSO_4$ to CaO

Greek symbols

Δr_i size interval of population i (m)
ε_0 sorbent initial porosity
ρ solid concentration (kg m^{-3})
ρ_b solid concentration in the bottom region (kg m^{-3})
ρ_c average density of char (kg m^{-3})
ρ_{CaO} density molar of CaO (mol m^{-3})
$\rho_{d,b}$ solid concentration due to the dispersed phase in the upper portion of the bottom region (kg m^{-3})
ρ_{exit} solid concentration at the gas outlet (kg m^{-3})
$\tau(r_i)$ residence time of particle size r_i (s)
τ_{diff2} time to reach the maximum sorbent sulfation conversion with the reaction controlled by gas diffusion through the product layer (s)

Subscripts

cc carbon in the core
cl carbon in the bottom and splash regions
i relative to the differential element at height h in the transport region
O_2 oxygen
S sulfur

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